

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
21 June 2001 (21.06.2001)

PCT

(10) International Publication Number
WO 01/44362 A1

(51) International Patent Classification⁷: C08K 5/32, 5/10, 5/526

(21) International Application Number: PCT/IB00/01830

(22) International Filing Date: 8 December 2000 (08.12.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/465,851 17 December 1999 (17.12.1999) US

(71) Applicant: BASELL TECHNOLOGY COMPANY BV
[NL/NL]; Hoeksteen 66, NL-2132 MS Hoofddorp (NL).

(72) Inventor: BECKER, Ronald, F.; 206 E. Seneca Drive,
Newark, DE 19702 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— With international search report.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 01/44362 A1

(54) Title: OLEFIN POLYMER COMPOSITION HAVING LOW SMOKE GENERATION AND FIBER, FILM AND FABRIC PREPARED THEREFROM

(57) Abstract: A polymer composition and fiber or film prepared therefrom, which contains i) an olefin polymer containing an acid neutralizing agent other than a metallic salt of a saturated or unsaturated fatty acid, and ii) a stabilizer system distributed throughout the polymer, the stabilizer system including (a) a phosphite selected from 2,2',2''-nitrilo[triethyl-tris(3,3',5,5'-tetra-tert-butyl-1,1-biphenyl-2,2'-diyl)phosphite] and tris(2,4-di-tert-butylphenyl) phosphite; and (b) a saturated hydrocarbon amine oxide. Also disclosed is a method for preparing a polyolefin fiber or film, which includes adding the above stabilizer system to an olefin polymer containing such an acid neutralizing agent. In a special embodiment, an unconventionally low amount of a saturated or unsaturated fatty acid may be present as a processing aid.

**TITLE: OLEFIN POLYMER COMPOSITION HAVING LOW SMOKE
GENERATION AND FIBER, FILM AND FABRIC PREPARED
THEREFROM**

BACKGROUND OF THE INVENTION:

5 Olefin polymers, especially polypropylene, are commonly spun into fibers, film or sheet by extruding molten polymer through die orifices such as a spinnerette, film or sheet dies, quenching the molten filament, film or sheet, orienting the filament, fiber or sheet, and heat setting the oriented filament, film or sheet prior to winding upon a bobbin. Woven and non-woven fabric are commonly made from such filament, film or sheet.

10 A problem associated with polyolefins produced using Ziegler-Natta type catalysts is the generation of visible "smoke" during melt extrusion of polyolefin during fiber spinning and film extrusion operations. The "smoke" evolves at the die, and is believed to comprise volatile organic compounds in the 20-50 carbon atom range. These evolved volatile organic compounds subsequently condense and coat equipment with resultant problems of non-
15 uniformity of nonwoven fabrics formed from such fibers or of films due to die deposits caused by the volatile organic compounds.

The incorporation of various additives into and/or onto olefin polymer materials to improve thermal stability, UV resistance, and processability is known. For example, the inclusion of an acid neutralizing agent in olefin polymer compositions is necessary due to
20 small amounts of catalyst residues contained within the olefin polymer. These catalyst residues can cause corrosion of processing equipment such as mold surfaces and die lips. The addition of an appropriate acid neutralizing agent can eliminate or at least reduce the potential for corrosion due to such residues.

However, the selection of acid neutralizing agent is important because it can affect the

overall acidity/basicity of an olefin polymer composition and influence the reactions of many of the organic additives in the polymer composition. In addition, the polyolefin's release properties can be affected by the acid neutralizing agent.

In practice, metallic stearates such as sodium, calcium and zinc are commonly added to olefin polymer materials as an acid neutralizing agent, with calcium stearate being the most common. Although other acid neutralizing agents are known, calcium stearate is predominately used because it functions as an external lubricant and processing aid in addition to acting as an acid neutralizing agent.

Phosphite compounds, including 2,2',2''-nitrilo[triethyl-tris (3,3',5,5'-tetra-tert-butyl-1,1-biphenyl-2,2'-diyl)phosphite] are typically added to polyolefin compositions to stabilize them against thermal and oxidative degradation. Various forms of 2,2',2''-nitrilo[triethyl-tris(3,3',5,5'-tetra-tert-butyl-1,1-biphenyl-2,2'-diyl)phosphite] are known. For example, U.S. Patent No. 5,326,802 discloses a beta crystalline modification of 2,2',2''-nitrilo[triethyl-tris(3,3',5,5'-tetra-tert-butyl-1,1-biphenyl-2,2'-diyl)phosphite]. Example 6 discloses the stabilization of polypropylene which also contains calcium stearate. U.S. Patents Nos. 5,331,031 and 5,405,893 disclose a gamma crystalline modification of 2,2',2''-nitrilo[triethyl-tris (3,3',5,5'-tetra-tert-butyl-1,1-biphenyl-2,2'-diyl)phosphite]. Example 4 illustrates the stabilization of polypropylene which also contains calcium stearate. An amorphous solid modification of 2, 2',2''-nitrilo[triethyl-tris(3,3',5,5'-tetra-tert-butyl-1,1-biphenyl-2, 2'-diyl)phosphite] is disclosed by U.S. Patent No. 5,276,076. Example 3 illustrates the stabilization of polypropylene which also contains calcium stearate.

U.S. Patent No. 5,834,541 discloses an olefin polymer composition having low smoke generation which contains an acid neutralizing agent other than a metallic salt of a saturated

or unsaturated fatty acid and a stabilizer system which includes a specified phosphite and a N,N-diakylhydroxylamine. The composition is particularly suitable for the manufacture of fibers and films.

U.S. Patent No. 5,844,029 discloses a thermoplastic composition containing a saturated hydrocarbon amine oxide and a second stabilizer which is broadly defined. There is no disclosure that the second stabilizer should be an acid neutralizing agent other than a metallic salt of a saturated or unsaturated fatty acid. The examples use a polypropylene containing calcium stearate.

An object of the invention is to provide an olefin polymer composition which generates a minimum amount of smoke during extrusion into a fiber or film.

Another object of the invention is to provide a low smoke olefin polymer composition which is stabilized against thermal and oxidative degradation, and the fiber, film or fabric prepared therefrom.

Yet another object of the invention is to provide a method for reducing volatile organic compounds generated during polyolefin fiber, film or fabric production by up to 90 percent.

BRIEF SUMMARY OF THE INVENTION:

In one aspect, the present invention relates to a polymer composition comprising:

- i) an olefin polymer containing an acid neutralizing agent other than a metallic salt of a saturated or unsaturated fatty acid, and
- ii) a stabilizer system distributed throughout the polymer, the stabilizer system comprising
 - (a) a phosphite selected from the group consisting of 2,2',2''-nitrilo[triethyl-

tris(3,3',5,5'-tetra-tert-butyl-1,1-biphenyl-2,2'-diyl)phosphite] and tris(2,4-di-tert-butylphenyl) phosphite] and

(b) a saturated hydrocarbon amine oxide.

In another aspect, the present invention relates to a polymer composition
5 comprising:

i) an olefin polymer containing an acid neutralizing agent other than a metallic salt of a saturated or unsaturated fatty acid,

ii) a processing aid comprising a metallic salt of a saturated or unsaturated fatty acid, the metallic salt of a saturated or unsaturated acid being present in a maximum amount of 200
10 ppm,

iii) a stabilizer system distributed throughout the polymer, the stabilizer system comprising

(a) a phosphite selected from the group consisting of 2,2',2''-nitrilo[triethyl-tris(3,3',5,5'-tetra-tert-butyl-1,1-biphenyl-2,2'-diyl)phosphite] and tris(2,4-di-tert-butylphenyl) phosphite] and
15 phosphite] and

(b) a saturated hydrocarbon amine oxide.

In another aspect, the present invention relates to a method for preparing an olefin polymer fiber or film, comprising

i) incorporating a stabilizer system into and/or onto an olefin polymer containing an
20 acid neutralizing agent other than calcium stearate, the stabilizer system comprising

(a) a phosphite selected from the group consisting of 2,2',2''-nitrilo[triethyl-tris(3,3',5,5'-tetra-tert-butyl-1,1-biphenyl-2,2'-diyl)phosphite] and tris(2,4-di-tert-butylphenyl) phosphite] and

(b) a saturated hydrocarbon amine oxide,
thereby producing a stabilized olefin polymer; and

ii) extruding the stabilized olefin polymer through a die, thereby producing an olefin polymer fiber, film or sheet.

5 **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS:**

The inventor has unexpectedly discovered that smoke generation during fiber, film and sheet processing can be significantly reduced by using (1) a combination of a saturated hydrocarbon amine oxide and a specific phosphite stabilizer to melt stabilize a controlled rheology olefin polymer, and (2) an acid neutralizing agent other than a metallic salt of a saturated or unsaturated fatty acid. A special embodiment of the invention provides a carefully tailored polyolefin composition which (1) employs an acid neutralizing agent other than a metallic salt of a saturated or unsaturated fatty acid, (2) contains an unconventionally low amount of calcium stearate which is ineffective to function as an acid neutralizer, and (3) contains a stabilizer system comprising selected phosphites and a saturated hydrocarbon amine oxide acts to reduce the smoke generated by the presence of the calcium stearate. The resulting composition has acceptable processing characteristics typical of polyolefins containing conventional amounts of calcium stearate, while producing significantly less smoke during extrusion into fiber or film than polyolefin compositions containing conventional amounts of calcium stearate.

20 Controlled rheology olefin polymers are prepared by polymerizing olefin monomers to a relatively high weight average molecular weight, which are then treated with peroxide to reduce their molecular weight to a desired average ("visbroken"). Alternately, controlled rheology polymers can be prepared by employing a Ziegler-Natta catalyst system known to

provide the desired weight average molecular weight and by using a sufficient amount of chain transfer agent, such as hydrogen, during the polymerization to achieve the desired melt flow rate.

The olefin polymer is derived by polymerizing at least one mono- α -olefin, such as ethylene, propylene, isobutylene, butene-1, 3-methyl-1-butene and 4-methyl-1-pentene. Polyethylene, both homopolymer and copolymer, may be for example medium density, high density or linear low density polyethylene.

Copolymers of mono- α -olefins may also be used in the instant compositions, for example ethylene/propylene copolymers, propylene/butene-1 copolymers, propylene/octene-1 copolymers, ethylene/butene-1 copolymers, ethylene/octene-1 copolymers as well as ethylene/vinyl acetate copolymers.

Heterophasic or impact modified olefin polymers may also be used in the compositions of this invention. Suitable heterophasic olefin polymers include

a) an olefin polymer composition comprising:

- (i) about 10 parts to about 60 parts by weight of a crystalline propylene homopolymer having an isotactic index greater than 80, or a crystalline copolymer selected from the group consisting of (a) propylene and ethylene, (b) propylene, ethylene and a C_4 - C_8 α -olefin, and (c) propylene and a C_4 - C_8 α -olefin, the copolymer having a propylene content of more than 85% by weight and an isotactic index greater than 85;
- (ii) about 5 parts to about 25 parts by weight of a copolymer of ethylene and propylene or a C_4 - C_8 α -olefin that is insoluble in xylene at ambient temperature; and

(iii) about 30 parts to about 70 parts by weight of an elastomeric copolymer selected from the group consisting of (a) ethylene and propylene, (b) ethylene, propylene, and a C₄-C₈ α -olefin, and (c) ethylene and a C₄-C₈ α -olefin, the copolymer optionally containing about 0.5% to about 10% by weight of a diene, and containing less than 70% by weight of ethylene and being soluble in xylene at ambient temperature and having an intrinsic viscosity of about 1.5 to about 4.0 dl/g;

the total of (ii) and (iii), based on the total olefin polymer composition being from about 50% to about 90%, and the weight ratio of (ii)/(iii) being less than 0.4, wherein the composition is prepared by polymerization in at least two stages and has a flexural modulus of less than 150 MPa;

(b) an olefin polymer comprising:

- (i) about 10% to about 60% of a propylene homopolymer having an isotactic index greater than 80, or a crystalline copolymer selected from the group consisting of (a) ethylene and propylene, (b) ethylene, propylene and a C₄-C₈ α -olefin, and (c) ethylene and a C₄-C₈ α -olefin, the copolymer having a propylene content greater than 85% and an isotactic index greater than 85;
- (ii) about 20% to about 60% of an amorphous copolymer selected from the group consisting of (a) ethylene and propylene, (b) ethylene, propylene, and a C₄-C₈ α -olefin, and (c) ethylene and a C₄-C₈ α -olefin, the copolymer optionally containing about 0.5% to about 10% of a diene and containing less than 70% ethylene and being soluble in xylene at ambient temperature; and

- (iii) about 3% to about 40% of a copolymer of ethylene and propylene or a C₄-C₈ α -olefin that is insoluble in xylene at ambient temperature;

wherein the composition has a flexural modulus of greater than 150 but less than 1200 MPa, preferably 200 to 1100 MPa, most preferably 200 to 1000 MPa; and

(c) an olefin polymer composition comprising:

(i) about 30% to about 98% of a polymeric material selected from the group consisting of a polypropylene homopolymer having an isotactic index greater than 90, and a crystalline copolymer having an isotactic index greater than 85 of propylene and at least one α -olefin of the formula CH₂=CHR, where R is H or a C₂-C₆ alkyl group, the α -olefin being less than 10% of the copolymer when R is H and being less than 20% when R is a C₂-C₆ alkyl group or a combination thereof with R=H, and

(ii) about 2% to about 70% of an elastomeric copolymer of propylene and an α -olefin of the formula CH₂=CHR, where R is H or a C₂-C₈ alkyl group, the α -olefin being about 45% to about 75% of the elastomeric copolymer, and about 10% to about 40% of the elastomeric copolymer being insoluble in xylene at ambient temperature, or an elastomeric copolymer of ethylene and a C₄-C₈ α -olefin having an α -olefin content of about 15% to about 60%.

As used herein, room or ambient temperature is approximately 25°C.

The total amount of polymerized ethylene in (a) is preferably about 10 to about 40% by weight.

The C₄₋₈ α -olefins useful in the preparation of (a) and (b) include, for example, butene-1; pentene-1; hexene-1; 4-methyl-1-pentene, and octene-1.

The diene, when present, is typically a butadiene, 1,4-hexadiene; 1,5-hexadiene, or ethyldenenorbornene.

Propylene polymer materials (a) and (b) can be prepared by polymerization in at least two stages, where in the first stage the propylene, or propylene and ethylene or an α -olefin, or propylene, ethylene and an α -olefin are polymerized to form component (i) of (a) or (b), and in the following stages the mixtures of ethylene and propylene or the α -olefin, or ethylene, propylene and the α -olefin, and optionally a diene, are polymerized to form components (ii) and (iii) of (a) and (b).

The polymerization of (a) and (b) can be conducted in liquid phase, gas phase, or liquid-gas phase using separate reactors, all of which can be done either by batch or continuously. For example, it is possible to carry out the polymerization of component (i) using liquid propylene as a diluent, and the polymerization of components (ii) and (iii) in gas phase, without intermediate stages except for the partial degassing of the propylene. All gas phase is the preferred method.

The preparation of propylene polymer material (a) is described in more detail in U.S. Patents No. 5,212,246, which preparation is incorporated herein by reference. The preparation of propylene polymer material (b) is described in more detail in U.S. Patents Nos. 3,302,454 and 5,409,992, which preparation is incorporated herein by reference.

The polymer composition (c) can be obtained by sequential polymerization of monomers in the presence of Ziegler-Natta catalysts, or by mechanical blending of components (i) and (ii). Such a sequential polymerization is described in more detail in U.S. Patent No. 5,486,419, which preparation is incorporated herein by reference.

The sequential polymerization can also be carried out with a mixture of Ziegler-Natta and metallocene catalysts or by using a Ziegler-Natta catalyst in one reactor, preferably the first reactor, and a metallocene catalyst in the other reactor(s), preferably the reactor(s) after the first reactor.

5 Mixtures of the homopolymers or mixtures of olefin copolymers or mixtures of both can be used.

The olefin polymer is preferably a crystalline propylene polymer, most preferably either a crystalline propylene homopolymer having an isotactic index greater than 90, most preferably greater than 93, or a crystalline, random copolymer of propylene and either
10 ethylene or C₄-C₁₀ α -olefin with an isotactic index greater than 85. The propylene polymer is preferably visbroken to a melt flow rate ("MFR") of 15-50 g/10 minutes, most preferably 25-38 g/10 minutes, measured according to ASTM 1238, Condition L. Such propylene polymers are commercially available from Basell USA Inc. (f/k/a Montell USA Inc.).

The process of visbreaking a propylene polymer material is well known to those
15 skilled in the art. Generally, it is performed as follows: propylene polymer in particulate form, e.g., "as polymerized" flake or pelletized, has sprayed thereon or blended therewith, a prodegradant or free radical generating source, e.g., a peroxide in liquid or powder form or absorbed on and/or in a carrier, e.g., polypropylene/peroxide concentrate. The propylene polymer and peroxide or propylene polymer/peroxide concentrate is then introduced into a
20 means for thermally plasticizing or melt blending and conveying the mixture, e.g., an extruder at elevated temperature. Residence time and temperature are controlled in relation to the particular peroxide selected (i.e., based on the half-life of the peroxide at the process temperature of the extruder) so as to effect the desired degree of polymer chain degradation.

The net result is to narrow the molecular weight distribution of the propylene polymer as well as to reduce the overall molecular weight and thereby increase the MFR relative to the as-polymerized propylene polymer. For example, a propylene polymer with a fractional MFR (i.e., less than 1), or a propylene polymer with a MFR of 0.5-10 g/10 minutes, can be selectively visbroken to a MFR of 15-50, preferably 25-38 g/10 minutes, by selection of peroxide type, extruder temperature and extruder residence time without undue experimentation. Sufficient care should be exercised in the practice of the procedure to avoid crosslinking in the presence of an ethylene-containing copolymer; typically, crosslinking will be avoided where the ethylene content of the copolymer is sufficiently low.

The polymer composition of the present invention contains an acid neutralizing agent other than a metal salt of a saturated or unsaturated fatty acid, particularly, metallic stearates and especially calcium stearate. Fatty acids typically have 4 to 22 carbon atoms with a terminal carboxyl group (COOH). Typical metals are those in Group Ia and II of the Periodic Table.

Suitable acid neutralizing compounds for use in the present invention include zeolite structures (hydrotalcite, both natural and synthetic), aluminum silicate, calcium carbonate, sodium benzoate and oxides and hydroxides of Group IA and IIA metals. Calcium lactate, calcium hydroxide, calcium oxide or mixtures thereof are most preferred. Hydrotalcite, which typically contains 3-10% by weight calcium stearate, based on the weight of hydrotalcite, may be employed if its calcium stearate contribution is taken into account in adjusting the amount of calcium stearate present in the polyolefin composition.

An effective amount of the acid neutralizing agent will range from 200 to 2000 ppm polymer, preferably 200 to 1,000 ppm polymer, depending on the acidity of the polyolefin and the equivalent weight of the acid neutralizing agent. In the case of polypropylene, a preferred amount of an acid neutralizing agent such as calcium lactate ranges from 200 to 300 ppm polymer.

A special embodiment of the present invention contains an unconventionally low amount of a metallic salt of a saturated or unsaturated fatty acid, which is present in a maximum amount of 200 ppm. Calcium stearate is preferred, and is preferably present in an amount of from 100 to 200 ppm, still more preferably in an amount of from 125 to 175 ppm.

Without wishing to be bound by any theory of the invention, it is currently believed that the acid neutralizing agent may act alone or in concert with the unconventionally low amount of calcium stearate to neutralize acids present in the polymer. More particularly, the effective amount of the acid neutralizing agent may depend upon the equivalent weight of the specific acid neutralizing agent chosen together with the amount of calcium stearate processing aid present in the polymer.

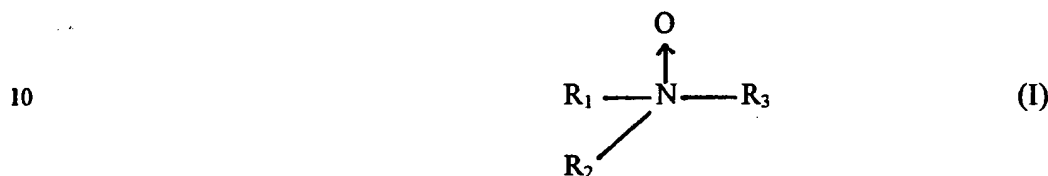
Thus, the calcium stearate may possess a dual function by (1) serving as a processing agent and (2) acting in concert with the acid neutralizing agent to neutralize acids contained within the polymer composition. Importantly, the amount of calcium stearate, by itself, is insufficient to completely neutralize the acids present in the polymer composition.

The phosphite stabilizer can be either 2,2',2''-nitrilo [triethyl-tris(3,3',5,5'-tetra-tert-butyl-1,1-biphenyl-2,2'-diyl) phosphite] or tris(2,4-di-tert-butylphenyl) phosphite. Both of

these compounds are commercially available. The preparation of 2,2',2''-nitrilo[triethyl-tris(3,3',5,5'-tetra-tert-butyl-1,1-biphenyl-2,2'-diyl)phosphite] is disclosed in U.S. Patent No. 4,318,845, the disclosure of which is incorporated herein by reference in its entirety.

Amine oxides and processes for making thereof are set out in Richard J. Nadolsky, 5
Amine Oxides, Encyclopedia of Chemical Technology, Vol. 2, pages 259-271, John Wiley & Sons, Inc. (1978), which is incorporated herein by reference.

The amine oxide is preferably a saturated tertiary amine oxide which conforms to formula (I):



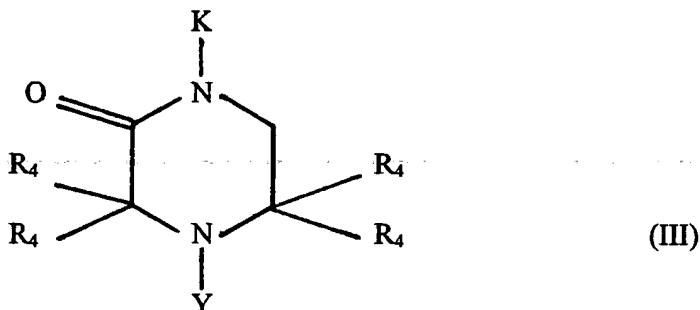
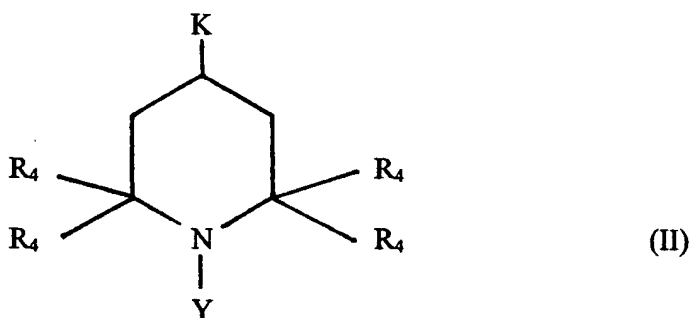
wherein R₁ and R₂ are independently each a C₆ to C₃₆ residue that may optionally contain at least one -O-, -S-, -SO-, -CO₂-, -CO-, or -CON- moiety; and

R₃ is a C₁ to C₃₆ residue that may also optionally and independently contain at least 15
one -O-, -S-, -SO-, -CO₂-, -CO-, or -CON- moiety.

Included in the residues for R₁, R₂, and R₃ are benzyl and substituted benzyl residues. It is also possible for each of R₁, R₂, and R₃ to be the same residue. R₁ and R₂ are preferably C₈ to C₂₆ residues and most preferably C₁₀ to C₂₆ residues and R₃ is preferably C₁ to C₂₂ residues and most preferably methyl. Also, preferred amine oxides include those wherein R₁, 20
R₂, and R₃ are the same C₆ to C₃₆ residues. Preferably, all of the aforementioned residues for R₁, R₂, and R₃ are saturated hydrocarbon residues or saturated hydrocarbon residues containing at least one of the aforementioned -O-, -S-, -SO-, -CO₂-, -CO-, or -CON- moieties.

The saturated amine oxide of the present invention also includes poly(amine oxides). By poly(amine oxide) is meant tertiary amine oxides containing at least two tertiary amine oxides per molecule. Illustrative poly(amine oxides) (also called "poly(tertiary amine oxides)") include the tertiary amine oxide analogues of aliphatic and alicyclic diamines such as, for example, 1,4-diaminobutane; 1,6-diaminohexane; 1,10-diaminodecane; and 1,4-diaminocyclohexane, and aromatic based diamines such as, for example, diamino anthraquinones and diaminoanisoles. Also included are tertiary amine oxides derived from oligomers and polymers of the aforementioned diamines. Useful amine oxides also include amine oxides attached to polymers, for example, polyolefins, polyacrylates, polyesters, polyamides, polystyrenes, and the like. When the amine oxide is attached to a polymer, the average number of amine oxides per polymer can vary widely as not all polymer chains need to contain an amine oxide. Generally a useful number of amine oxide moieties in the overall thermoplastic resin is between about 0.001 weight percent and about 5 weight percent, based on the weight of the entire thermoplastic composition. All of the aforementioned amine oxides may optionally contain at least one -O-, -S-, -SO-, -CO₂-, -CO-, or -CON- moiety. In a preferred embodiment, each tertiary amine oxide of the polymeric tertiary amine oxide contains a C₁ residue.

In a preferred embodiment of the present invention, the saturated amine oxide is attached to a molecule containing a hindered amine. Hindered amines are known in the art and the amine oxide of the present invention may be attached to the hindered amine in any manner and structural position of the hindered amine. Useful hindered amines in the present invention include those of the general formulas (II) and (III):



wherein K is a carbon chain containing the amine oxide (or amine oxides),

Y is a C₁₋₃₀ alkyl moiety, a -C(O)R moiety wherein R is a C₁₋₃₀ alkyl group, or a -OR moiety wherein R is a C₁₋₃₀ alkyl group, and each R₄ is independently a C₁₋₃₀ alkyl group, preferably a methyl group. Also included are amine oxides containing more than one hindered

15 amine and more than one saturated amine oxide per molecule. The hindered amine may be attached to a poly(tertiary amine oxide) or attached to a polymeric substrate, as discussed above.

Also included in the present invention are the thermal reaction products of tertiary amine oxides. Under elevated temperatures, e.g., such as those useful to prepare the

20 thermoplastic compositions of the present invention, amine oxides including those illustrated by Formula I, are believed to undergo various reactions which are believed to produce hydroxyl amines and olefinic species. Amine oxide reaction products containing at least one long chain carbon residue are preferred in order to increase the solubility of the reaction

products, including the hydroxyl amine-type reaction products, with the thermoplastic resin. When only a single alkyl substituent (i.e., only one of R_1 , R_2 , and R_3) in the tertiary amine oxide is a C_6 to C_{36} residue and the other two alkyl substituents are C_{1-5} residues, some of the hydroxyl amine-type reaction products are believed to contain only short chain substituents (i.e., C_{1-5} residues). It is believed that this is a result of some of the long chain residues being eliminated from the amine oxide as an olefinic by-product. In order to insure that at least one long chain is retained in the hydroxyl amine-type thermal reaction products, either all three substituents should preferably be long chain or one chain can be C_1 (e.g., methyl) and the other two substituents be long chain (e.g., C_6 to C_{36} residues). When one substituent is a C_1 residue and the other two substituents are long chain residues (including polymeric residues as previously described), the resultant thermal reaction product will be asymmetrical and contain a C_1 residue and a long chain residue. By long chain carbon residue is meant from C_6 to about C_{36} , preferably from C_8 to C_{26} and most preferably C_{10} to C_{22} . Also included by long chain residue are the before mentioned polymeric amine oxide residues. The long chain carbon residue may also optionally contain at least one of the before mentioned -O-, -S-, -SO-, -CO₂-, -CO-, or -CON- moieties described for R_1 , R_2 , and R_3 . Hydroxyl amine-type reaction products that do not contain the aforementioned long chain residue tend to migrate out of the thermoplastic resin and can bloom to the surface of the thermoplastic resin or coat the surface of the processing equipment requiring costly downtime for cleaning and maintenance. It should be clear from the foregoing that the present invention includes amine oxides containing at least one long chain carbon residue, preferably asymmetrical amine oxides containing a long chain and a short chain; and also include polymeric amine oxides containing at least two amine oxides per molecule.

Preferred saturated amine oxides for use in the present invention include dioctylmethyl amine oxide, trioctyl amine oxide, didecylmethyl amine oxide, tridecyl amine oxide, di(coco alkyl) methyl amine oxide, tri(coco alkyl) amine oxide, di(tallow alkyl) methyl amine oxide, tri(tallow alkyl) amine oxide, tri(C₂₀-C₂₂) amine oxide, and di(C₂₀-C₂₂ alkyl) methyl amine
5 oxide. Preferred saturated hydroxyl amines include octyl methyl hydroxyl amine, decyl methyl hydroxyl amine, (coco alkyl) methyl hydroxyl amine, (tallow alkyl) methyl hydroxyl amine, and (C₂₀-C₂₂ alkyl) methyl hydroxyl amine. By the term "coco alkyl" is meant hydrogenated C₁₂-C₁₄ alkyl commonly referred to as hydrogenated coconut oil. By the term "tallow alkyl" is meant hydrogenated C₁₆-C₁₈ alkyl commonly referred to as hydrogenated tallow oil.

10 Hydrogenated tallow oil is described in U.S. Patent No. 4,876,300. The aforementioned hydrogenated coconut oil and hydrogenated tallow oil do contain some percentage of higher and/or lower carbon chain lengths than are described above and it should be understood that these other fractions are within the scope of the present invention. It is preferred that at least 75% of the carbon chains be within the described ranges for the coconut oil and tallow oil.

15 An effective amount of the stabilizer system will typically range from 250 to 2000 ppm polymer, with a preferred amount being 700 to 1500 ppm polymer. The stabilizer system may contain from 5 to 80% saturated hydrocarbon amine oxide, and 95 to 20% phosphite, preferably 5 to 45% and 95 to 55%, and most preferably 5 to 25% and 95 to 75 wt.%.

The stabilizer system of the present invention may also contain at least one other
20 stabilizer compound. For example, another phosphite compound may be used in partial substitution of the primary phosphite stabilizer compounds for economic reasons. However, the inventor has discovered that such a substitution can only be partial (i.e. around 50%); full replacement of the primary phosphite compounds will significantly increase smoke generation.

Suitable phosphite partial replacements include tris(2,4-di-tert-butylphenyl)phosphite and 2,4,6-tri-tert-butyl-phenyl-2-butyl-2-ethyl-1,3-propanediol phosphite.

The stabilizer system can also include conventional stabilizer compounds with little or no adverse affect on smoke generation. For example, a hindered amine light stabilizer (HALS) can be added to the stabilizer system. Suitable HALS include poly[6-[(1,1,3,3-tetramethyl-butyl)amino-s-triazine 2,4-yl][2,2,6,6-tetramethyl-4-piperidyl]imino]hexamethylene[(2,2,6,6-tetramethyl-4-piperidyl)imino] and 1,3,5-triazine-2,4,6,- triamine-N,N''-[1,2-ethanedylbis[N-(3-[4,6-bis-(butyl-1,2,2,6,6-pentamethyl-4-piperidiny]amine)propyl-[N,N-dibutyl-N,N-bis(1,2,2,6,6-pentamethyl-4-piperidiny)]. Similarly, phenolic stabilizers such as octadecyl-3,5-di-tert-butyl-4-hydroxyhydrocinnamate and tetrakis [methylene3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate]-methane may be added to increase thermal stability.

The stabilized polyolefin composition may contain other additives as appropriate for the intended use of the composition. Such additives include antistatic agents, flameproofing agents, antiblocking agents, lubricants, pigments, optical brighteners, nucleators and clarifiers.

The stabilizer system components may be incorporated into the olefin polymer in any conventional manner, such as by dry blending the stabilizer system directly with polymer pellets, by means of tumble mixers and Henschel blenders. Solutions, emulsions or slurries of the stabilizer system can be sprayed onto or admixed with granular polymer. For example, the stabilizer components can be coated upon granules of the olefin polymer in a fluidized bed according to the process of U.S. Pat. No. 5,141,772, the disclosure of which is incorporated herein in its entirety. The stabilizer components can also be blended with molten polymer by means of a Banbury mixer, Bradbender mixer, roll mill or screw extruder.

The stabilizer system can also be added to the olefin polymer in the form of a

masterbatch according to the conventional techniques discussed in U.S. Patent No. 5,236,962, the disclosure of which is incorporated by reference herein in its entirety.

5 The stabilized polyolefin composition of the present invention is particularly suitable for manufacture into a fiber or film using conventional techniques and apparatus. More particularly, the stabilized olefin polymer may be extruded at conventional temperatures (i.e., 210 to 280°C.) through a die, quenched, partially or fully oriented and heat-set prior to winding upon a bobbin or undergoing further processing into spunbonded or melt blown fiber, and ultimately into woven and non-woven webs.

10 As used herein the term "nonwoven web" means a web having a structure of individual fibers or threads which are interlaid, but not in an identifiable manner as in a knitted web. Nonwoven webs have been formed from many processes such as for example, meltblowing processes, spunbonding processes, and bonded carded web processes. The basis weight of nonwoven webs is usually expressed in ounces of material per square yard (osy) or grams per square meter (gsm) and the fiber diameters are usually expressed in microns.

15 As used herein the term "spunbonded fibers" refers to small diameter fibers which are formed by extruding molten thermoplastic material as filaments from a plurality of fine, usually circular capillaries of a spinneret with the diameter of the extruded filaments then being rapidly reduced as by, for example, in U.S. Patent Nos. 4,340,563, 3,692,618, 3,802,817, 3,338,992, 3,341,394, 3,502,763 and 3,542,615. Spunbond fibers are generally
20 not tacky when they are deposited onto a collecting surface. Spunbond fibers are generally continuous and have average diameters (from a sample of at least 10) larger than 7 microns, more particularly, between about 10 and 20 microns.

As used herein the term "meltblown fibers" means fibers formed by extruding a molten thermoplastic material through a plurality of fine, usually circular, die capillaries as molten threads or filaments into converging high velocity, usually hot, gas (e.g., air) streams which attenuate the filaments of molten thermoplastic material to reduce their diameter, which may be to microfiber diameter. Thereafter, the meltblown fibers are carried by the high velocity gas stream and are deposited on a collecting surface to form a web of randomly dispersed meltblown fibers. Such a process is disclosed in U.S. Patent No. 3,849,241. Meltblown fibers are microfibers which may be continuous or discontinuous, are generally smaller than 10 microns in average diameter, and are generally tacky when deposited onto a collecting surface. U.S. Patent No. 5,667,562 discloses the production of filter media from polypropylene-based fibers using a spunbond process and is incorporated herein by reference.

A particularly preferred polypropylene resin composition contains 800 ppm 2,2',2''-nitrilotriethyl-tris(3,3',5,5'-tetra-tert-butyl-1,1-biphenyl-2,2'-diyl) phosphite, 500 ppm methyl(di-C₁₄₋₂₂)amine oxide; 500 ppm tetrakis[methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)] methane, and 250 ppm calcium lactate as an acid neutralizing agent.

EXAMPLE:

This Example is presented for the purpose of illustration only, and should not be construed to limit the nature or scope of the invention disclosed herein in any manner whatsoever.

The chemical identities of the products used in the formulations below are as follows:

Phosphite

Irgafos 12 [2,2',2''-nitrilo[triethyl-tris(3,3',5,5'-tetra-tert-butyl-1,1-biphenyl-2,2'-diyl)phosphite], commercially available from Ciba Specialty Chemicals Corporation.

Amine Oxide

Genox EP N,N-di(C₁₄₋₂₂)amine oxide, commercially available from General Electric Specialty Chemicals.

Miscellaneous:

5 Pationic 1240 calcium lactate, commercially available from American Ingredients Company.

Lupersol 101 2,5-dimethyl-2,5-di-(t-butylperoxy)hexane, commercially available from Elf Atochem North America, Inc.

All amounts in this specification are reported as parts by weight unless otherwise indicated.

Example I

10 Three sample formulations were prepared based on a polypropylene feedstock prepared from a commercially produced polypropylene flake having an xylene soluble content at room temperature of 4.0% and an initial MFR of 1.5 g/10 minutes, measured according to ASTM 1238, Condition L, and visbroken to a target MFR of 35 g/10 minutes.

15 The sample formulations were then mixed together, extruded and pelletized. Samples of each formulation were evaluated for smoke generation and yellowness index.

Smoke generation is measured by extruding 10 pound samples of each formulation at a rate of 10 pounds/hour. Volatile organic compounds are measured and recorded from evolved smoke aspirated from the die orifice via a vacuum system to a sample chamber where a laser particle counter measures the concentration of volatile particles in milligrams per cubic
20 meter.

Color is measured according to ASTM-D 1925-70, Section I, using a Hunter D25P-2 calorimeter in the total transmission mode, which is first standardized using air as a reference.

Yellowness is defined as the deviation from whiteness in the dominant wavelength range from 570 to 580 nm. The yellowness index (YI) is a measure of the magnitude of yellowness relative to a magnesium oxide standard reference. The lower the number the better the color.

Table 1

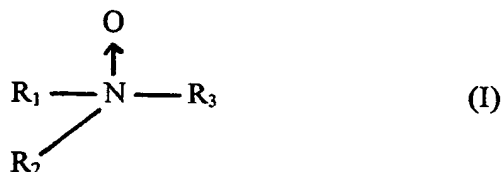
Component	I-1	I-2	I-3
Polypropylene	100	100	100
GENOX EP amine oxide	-	0.04	0.04
Ca stearate	0.05	-	-
Irgafos 12 phosphite	-	-	0.08
Pationic 1240 lactate	-	0.025	0.025
Lupersol 101 peroxide	**	**	**
MFR, g/10 min.	64.1	41.9	40.1
Smoke, mg/m ³	240	180	9.5
Yellowness Index	-0.47	-0.18	-0.58

5 Examination of Table I illustrates the dramatic reduction in volatile organic compound generation exhibited by the combination of an amine oxide and a phosphite stabilizer. More particularly, inventive sample I-3 achieved a significant reduction in volatile organic compound generation in comparison to control sample I-1, which contains a conventional amount of calcium stearate (550 ppm) but no stabilizer, and control sample I-2, which
10 contains the amine oxide and a non-calcium stearate acid scavenger, but does not contain a phosphite stabilizer.

Other features, advantages and embodiments of the invention disclosed herein will be readily apparent to those exercising ordinary skill after reading the foregoing disclosures. In this regard, while specific embodiments of the invention have been described in considerable detail, variations and modifications of these embodiments can be affected without departing
5 from the spirit and scope of the invention as described and claimed.

1. A polymer composition comprising
 - (i) an olefin polymer containing an acid neutralizing agent other than a metallic salt of a saturated or unsaturated fatty acid, and
 - ii) a stabilizer system distributed throughout said polymer, said stabilizer system
- 5 comprising
 - (a) a phosphite selected from the group consisting of 2,2',2''-nitrilo[triethyl-tris(3,3',5,5'-tetra-tert-butyl-1,1-biphenyl-2,2'-diyl)phosphite] and tris(2,4-di-tert-butylphenyl) phosphite; and
 - (b) a saturated hydrocarbon amine oxide.
- 10 2. The polymer composition of claim 1, wherein said acid neutralizing agent is at least one member selected from the group consisting of hydrotalcites, aluminum silicate, and oxides and hydroxides of Group II metals.
3. The polymer composition of claim 2, wherein said acid neutralizing agent is selected from the group consisting of calcium lactate, calcium hydroxide, calcium oxide and mixtures
- 15 thereof.
4. The polymer composition of claim 1, wherein said phosphite is 2,2',2''-nitrilo[triethyl-tris(3,3',5,5'-tetra-tert-butyl-1,1-biphenyl-2,2'-diyl)phosphite].

5. The polymer composition of claim 1, wherein said amine oxide conforms to the formula (I):



5

wherein R₁, R₂, and R₃ are independently selected from alkyl, aryl, aralkyl, alkaryl, cycloalkyl, alkycycloalkyl and cycloalkalkyl and each have from 1 to 36 carbon atoms per group, provided that if one of R₁, R₂ and R₃ is an alkyl group having from 6 to 36 carbon atoms per group, then the other two of R₁, R₂ and R₃ cannot both be alkyl groups having from 1 to 5 carbon atoms per group;

10

6. The polymer composition of claim 5, wherein said hydrocarbon amine oxide is a trialkyl amine oxide.
7. The polymer composition of claim 5, wherein said amine oxide is tri(C₁₂-C₂₂)amine oxide.
- 15 8. The polymer composition of claim 5, wherein an amount of amine oxide effective to stabilize the thermoplastic resin is admixed with the thermoplastic resin.
9. The polymer composition of claim 1, wherein said stabilizer system is present in an amount of 250 to 2000 ppm polymer.

10. The polymer composition of claim 9, wherein said stabilizer system is present in an amount of from 700 to 1500 ppm polymer.
11. The polymer composition of claim 1, wherein said stabilizer system comprises 10 to 80% saturated hydrocarbon amine oxide and 90 to 20% phosphite.
- 5 12. The polymer composition of claim 1, further comprising
(c) at least one other stabilizer compound, said other stabilizer comprising at least one member selected from the group consisting of a phenol, a hindered amine and a phosphite other than 2,2',2''-nitrilo[triethyl-tris(3,3',5,5'-tetra-tert-butyl-1,1- biphenyl-2,2'-diyl)phosphite] or tris(2,4-di-tert-butylphenyl) phosphite.
- 10 13. The polymer composition of claim 1, wherein said olefin polymer is either a crystalline propylene homopolymer having an isotactic index greater than 90 or a crystalline, random copolymer of propylene and either ethylene or C₄-C₁₀ α -olefins.
14. The polymer composition of claim 1 further comprising a processing aid comprising a metallic salt of a saturated or unsaturated fatty acid, the metallic salt of a saturated or
15 unsaturated acid being present in a maximum amount of 200 ppm.
15. The polymer composition of claim 14, wherein said processing aid comprises calcium stearate in an amount of from 100 to 200 ppm.

16. The polymer composition of claim 15, wherein said calcium stearate is present in an amount of from 125 to 175 ppm.
17. A method for preparing an olefin polymer fiber or film, comprising
- i) incorporating a stabilizer system into an olefin polymer containing an acid neutralizing agent other than a metallic salt of a saturated or unsaturated fatty acid, said stabilizer system comprising
- (a) a phosphite selected from the group consisting of 2,2',2''-nitrido[triethyl-tris(3,3',5,5'-tetra-tert-butyl-1,1-biphenyl-2,2'-diyl)phosphite] and tris(2,4-di-tert-butylphenyl) phosphite; and
- (b) a saturated hydrocarbon amine oxide, thereby producing a stabilized olefin polymer; and
- ii) extruding said stabilized olefin polymer through a die, thereby producing an olefin polymer fiber or film.
18. A fiber produced according to the method of claim 17.
19. A film produced according to the method of claim 17.
20. A fabric comprising a plurality of fibers of claim 18.
21. The fabric of claim 20, wherein said fabric is a non-woven fabric prepared using a spunbond or meltblown process.

INTERNATIONAL SEARCH REPORT

Int. Application No

PCT/IB 00/01830

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08K5/32 C08K5/10 C08K5/526

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 875 530 A (MONTELL NORTH AMERICA INC) 4 November 1998 (1998-11-04) cited in the application examples I-7	1-21
Y	EP 0 867 467 A (GEN ELECTRIC) 30 September 1998 (1998-09-30) example 13	1-21
Y	US 5 844 029 A (PRABHU VAIKUNTH S ET AL) 1 December 1998 (1998-12-01) cited in the application claims 5-8	7

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

6 March 2001

Date of mailing of the international search report

23/03/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Schmidt, H

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. J. Application No

PCT/IB 00/01830

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0875530 A	04-11-1998	US 5834541 A	10-11-1998
		AU 6378298 A	05-11-1998
		BR 9801528 A	29-06-1999
		CA 2236634 A	02-11-1998
		CN 1198448 A	11-11-1998
		CZ 9801330 A	11-11-1998
		HU 9800914 A, B	30-11-1998
		JP 10306178 A	17-11-1998
		NO 981917 A	03-11-1998
		PL 326099 A	09-11-1998
		SK 48498 A	04-11-1998
EP 0867467 A	30-09-1998	US 5922794 A	13-07-1999
		CN 1195671 A	14-10-1998
		JP 10338815 A	22-12-1998
		ZA 9802113 A	14-09-1998
US 5844029 A	01-12-1998	AU 716557 B	02-03-2000
		AU 7244496 A	17-04-1997
		BR 9606656 A	30-09-1997
		CA 2205911 A	03-04-1997
		CN 1168147 A	17-12-1997
		CZ 9701581 A	12-11-1997
		EP 0793688 A	10-09-1997
		JP 10510584 T	13-10-1998
		NO 972345 A	16-07-1997
		PL 320364 A	29-09-1997
		TR 9700407 T	23-08-1999
		US 6103798 A	15-08-2000
		WO 9711993 A	03-04-1997
		US 5880191 A	09-03-1999
		HU 9801389 A	30-11-1998